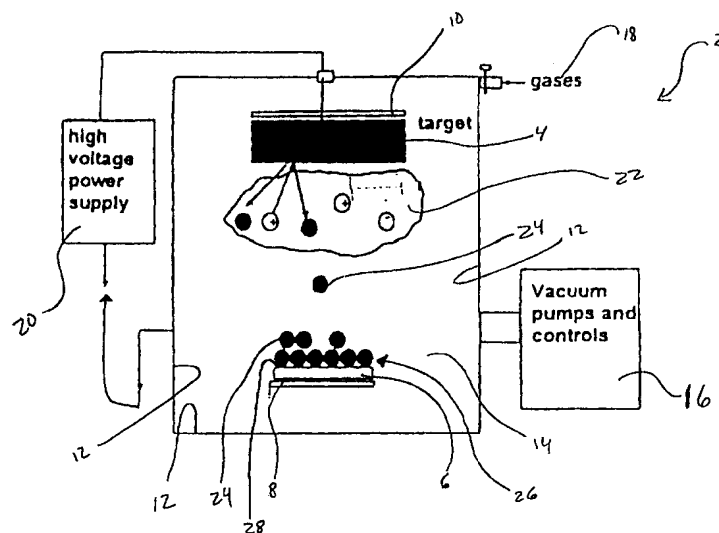


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(54) Title: SPUTTER-DEPOSITED FUEL CELL MEMBRANES AND ELECTRODES**(57) Abstract**

A method for preparing a membrane for use in a fuel cell electrode assembly includes the steps of providing an electrolyte membrane, and sputter-depositing a catalyst onto the electrolyte membrane. The sputter-deposited catalyst may be applied to multiple sides of the membrane. A method for forming an electrode for use in a fuel cell membrane electrode assembly includes the steps of obtaining a catalyst, obtaining a backing, and sputter depositing the catalyst onto the backing. In the sputtering operation, the electrolyte membrane or the backing forms a substrate (6), while the catalyst is deposited from a target (4). The membranes and electrodes are useful for assembling fuel cells that include an anode, a cathode, a fuel supply, and an electrolyte membrane, wherein the membrane includes a sputter-deposited catalyst, which is effective for sustaining a voltage across a membrane electrode assembly of the fuel cell.

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SPUTTER-DEPOSITED FUEL CELL MEMBRANES AND ELECTRODESStatement as to Federally Sponsored Research

The invention described herein was made in the performance of work under a NASA contact, and is subject
5 to the provisions of Public Law 96-517 (35 U.S.C. § 202)
in which the contractor has elected to retain title.

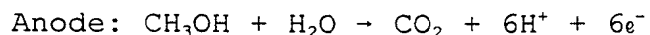
Field

The invention relates to chemical fuel cells.
More particularly, the invention relates to sputter-
10 depositing catalysts onto membranes and electrodes.

Background

Chemical fuel cells utilize renewable resources
and provide an alternative to burning fossil fuels to
generate power. Fuel cells utilize the
15 oxidation/reduction potentials of chemical reactions to
produce electrical current.

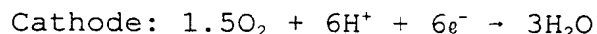
For example, methanol is a known example of a
renewable fuel source used in chemical fuel cells. In a
methanol driven fuel cell, methanol and water is
20 circulated past an anode that is separated from a cathode
by a membrane that is selectively permeable to protons.
The following chemical reaction takes place at the anode.



The protons generated at the anode pass through the
25 membrane to the cathode side of the fuel cell. The
electrons generated at the anode travel to the cathode
side of the fuel cell by passing through an external load
that connects the anode and cathode. Air or an

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alternative oxygen source is present at the cathode where the electro-reduction of oxygen occurs resulting in the following chemical reaction.



5 One of the important aspects of a chemical fuel cell is the membrane-electrode assembly (MEA). The MEA typically includes a selectively permeable polymer electrolyte membrane bonded between two electrodes, e.g., an anode electrode and a cathode electrode. Usually,
10 both the anode and the cathode each contain a catalyst, often a noble metal. Known processes for fabricating high performance MEAs involve painting, spraying, screen-printing and/or hot-bonding catalyst layers onto the electrolyte membrane and/or the electrodes. These known
15 methods can result in catalyst loading on the membrane and electrodes in the range from about 4 mg/cm² to about 12 mg/cm². Since noble metals such as platinum and ruthenium are extremely expensive, the catalyst cost can represent a large proportion of a fuel cell's total cost.
20 Therefore, there exists a need for reducing the amount of deposited catalyst, and hence the cost.

Summary of the Invention

In one aspect, the invention provides a method for preparing a membrane for use in a fuel cell membrane
25 electrode assembly that includes the steps of providing an electrolyte membrane, and sputter-depositing a catalyst onto the electrolyte membrane. In one embodiment, the electrolyte membrane further includes at least a first side and a second side wherein the catalyst
30 is applied to the first side and the second side of the electrolyte membrane.

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In another embodiment, the sputter-deposited catalyst is sputter-deposited to an anode side, a cathode side, or both the anode and the cathode side of the electrolyte membrane.

5 The methods for preparing a membrane include depositing ranges of catalyst weights including catalyst weights of less than about 1.0 mg of catalyst per square centimeter of the electrolyte membrane, catalyst weights of less than about 0.05 mg of catalyst per square
10 centimeter of electrolyte membrane, and catalyst weights ranging from about 0.05 mg of catalyst per square centimeter of the electrolyte membrane to about 1.0 mg of catalyst per square centimeter of the electrolyte membrane.

15 In another embodiment, the catalysts used in the methods for preparing a membrane include the transition metals. Further, the catalysts include mixtures of two or more catalysts, catalyst alloys and/or oxides thereof. The catalysts can be selected from Pt, Ru, Ni, Ti, Zr,
20 Sn, SnO₂, Os, Ir, W, WO₃, Pd, Mo, Nb, RuO₂, and Re.

In another embodiment, the catalysts are sputter-deposited as layers. Two or more catalysts may be sputter-deposited at the same time.

In another embodiment, the electrolyte membrane
25 further includes a first side and a second side wherein the catalyst further includes two or more catalysts, and wherein the two or more catalysts are sputter-deposited to at least one side of the electrolyte membrane.

In a second aspect, the invention provides a
30 method for forming an electrode for use in a fuel cell membrane electrode assembly that includes the steps of obtaining a catalyst, obtaining a backing, and sputter-depositing the catalyst onto the backing. In one

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embodiment, the backing is carbon paper. In other embodiments, the electrode is an anode or a cathode.

The methods for preparing an electrode include depositing ranges of catalyst weights including catalyst
5 weights of less than about 1.0 mg of catalyst per square centimeter of the backing, catalyst weights of less than about 0.05 mg of catalyst per square centimeter of backing, and catalyst weights ranging from about 0.05 mg of catalyst per square centimeter of the backing to about
10 1.0 mg of catalyst per square centimeter of the backing.

In another embodiment, the catalysts used in the methods for preparing an electrode include the transition metals. Further, the catalysts include mixtures of two or more catalysts, catalyst alloys and/or oxides thereof.
15 The catalysts can be selected from Pt, Ru, Ni, Ti, Zr, Sn, SnO₂, Os, Ir, W, WO₃, Pd, Mo, Nb, RuO₂, and Re.

In another embodiment, the catalysts are sputter-deposited as layers. Further, two or more catalysts may be sputter-deposited at the same time.

20 In a third aspect, the invention provides a fuel cell that includes an anode electrode, a cathode electrode, a fuel supply, and an electrolyte membrane, wherein the electrolyte membrane includes a sputter-deposited catalyst, and the sputter-deposited catalyst is
25 effective for sustaining a voltage across a membrane electrode assembly in the fuel cell.

In other embodiments, the catalyst is sputter-deposited to an anode side, a cathode side or both the anode side and the cathode side of the electrolyte
30 membrane.

In another embodiment, the fuel cell has various sputter-deposited catalyst weight ranges including catalyst weights that are less than about 1.0 mg of

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catalyst per square centimeter of the electrolyte membrane, less than about 0.05 mg of catalyst per square centimeter of the electrolyte membrane, and/or range from about 0.05 mg of catalyst per square centimeter of the electrolyte membrane to about 1.0 mg of catalyst per square centimeter of the electrolyte membrane. In another embodiment, the catalyst weights are found on the anode side of the electrolyte membrane, or the cathode side of the electrolyte membrane, or both the anode side and the cathode side of the electrolyte membrane.

In another embodiment, the catalysts used in the fuel cell include the transition metals. Further, the catalysts include mixtures of two or more catalysts, catalyst alloys and/or oxides thereof. The catalysts can be selected from Pt, Ru, Ni, Ti, Zr, Sn, SnO_2 , Os, Ir, W, WO_3 , Pd, Mo, Nb, RuO_2 , and Re.

In another embodiment, the catalysts are sputter-deposited as layers. Two or more catalysts may be sputter-deposited at the same time.

In another embodiment, the electrolyte membrane of the fuel cell includes a first side and a second side, wherein the catalyst further includes two or more catalysts, and wherein the two or more catalysts are sputter-deposited to at least one side of the electrolyte membrane.

In another embodiment, the fuel cells are fabricated as methanol fuel cells or hydrogen fuel cells.

Unless otherwise defined, all technical and scientific terms and abbreviations used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention pertains. In case of conflict, the present specification, including definitions, will control. Other features and advantages

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of the invention will be apparent from the following description of the preferred embodiments and from the claims.

Brief Description of the Drawings

5 FIG. 1 is a block diagram depicting a sputter-deposition chamber;

 FIG. 2 is a graph depicting the performance of direct methanol fuel cells using sputter-deposited anodes;

10 FIG. 3 is a graph depicting the anode polarization behavior of sputter-deposited Pt-Ru and Pt electrodes;

 FIG. 4 is a graph depicting a comparison between sputter-deposited anodes and conventional anodes; and

 FIG. 5 is graph depicting the catalyst utilization
15 for various types of catalyst layers.

Like reference numbers denote similar items.

Description of the Preferred Embodiments

 This embodiment involves preparing polymer membranes and electrodes for fabrication into membrane
20 electrode assemblies (MEAs) for use in chemical fuel cells. In particular, the embodiment provides fuel cells and methods for preparing membranes and electrodes that utilize catalysts that are sputter-deposited onto the membranes and/or electrodes.

25 An illustrative method for sputter-depositing a catalyst onto polymer electrolyte membrane includes the following steps. A suitable electrolyte polymer that has a low permeability for a fuel source, ionic conductivity and good electrochemical stability is cast into a
30 membrane and hydrated for fabrication into a MEA using known methods. Useful polymers include co-polymers of

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tetrafluoroethylene and perfluoropolyether sulfonic acid such as the membrane materials sold under the trademark NAFION (TM), perfluorinated sulfonic acid polymers such as the materials sold under the trademark ACIPLEX (TM),
5 polyethylene sulfonic acid polymers, polypropylene sulfonic acid polymers, polystyrene sulfonic acid polymers, polyketone sulfonic acids, polybenzimidazole doped with phosphoric acid, sulfonated polyether sulfones, and other polyhydrocarbon-based sulfonic acid
10 polymers. Further, the electrolyte membranes further include polymer composites or blends. An illustrative method for preparing a polymer electrolyte membrane, such as NAFION (TM), is disclosed in United States Patent 5,773,162, which is hereby incorporated by reference in
15 its entirety.

A hydrated electrolyte membrane is prepared for receiving a sputter-deposited catalyst by air drying the hydrated electrolyte membrane for about 24 hours and then vacuum drying the membrane for an additional 30-60
20 minutes.

The process of sputtering materials onto a substrate and the use of sputter-deposition chambers are known. Any type of sputter deposition method may be used. Briefly, a sputter-deposition chamber typically
25 operates by using a voltage differential to dislodge particles from a target material that then attach to a substrate forming a coating of the target material on the substrate material.

FIG. 1 depicts a block diagram of a sputter-
30 deposition chamber 2 that sputter-deposits a target 4 onto a substrate 6. A substrate holder 8 secures the substrate 6 within the chamber 2 between a target holder 10 and a chamber wall 12. Substrate 6 includes any

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material upon which sputter-deposition of a target 4 is sought. For example, a vacuum-dried electrolyte membrane such as a membrane fabricated using a NAFION (TM) polymer is a useful substrate 6. It is to be understood that the
5 sputter-deposition chamber 2 also includes multiple substrates 6 in one chamber 2.

The target holder 10 secures a target 4 within the chamber 2. Although FIG. 1 depicts a single target holder 10 and target 4, it is to be understood that
10 multiple target holders 10 and targets 4 can be disposed within the sputter-deposition chamber. Multiple target holders 10 are used to simultaneously sputter-deposit multiple target 4 materials onto at least one substrate 6. Target 4 materials include mixtures of materials,
15 e.g., metal alloys, that serve to sputter-deposit multiple target 4 materials onto at least one substrate 6. Useful targets 4 for preparing MEAs include catalysts used in chemical fuel cells. Useful catalysts include the transition metals, e.g., nickel (Ni), titanium (Ti),
20 zirconium (Zr), tin (Sn), tin oxides such as SnO₂, molybdenum (Mo), ruthenium (Ru), ruthenium oxides such as RuO₂, platinum (Pt), palladium (Pd), niobium (Nb), osmium (Os), iridium (Ir), tungsten (W), tungsten oxides such as WO₃, rhenium (Re), alloys thereof, and other similar
25 materials. Further, target 4 materials include any type of composition including single, binary, ternary, and quaternary compositions of individual target 4 materials.

After the target 4 and substrate 6 are secured, the chamber space 14 is evacuated using a vacuum pump and
30 controls 16 and then filled with a gas 18. Gas 18 includes inert gases such as argon, reactive gases, or mixtures of inert gases and reactive gases. Useful gas 18 pressures inside the chamber space 14 range from about

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5 millitorr to about 100 millitorr. The gas 18 pressure affects the deposition rate of the target 4 and the energy of the sputtered atoms or material that reach the substrate 6.

5 A sputter-deposition process for contacting the target 4 onto the substrate 6 is initiated using a power supply 20 to apply a voltage differential between the target 4 and the chamber wall 12. Useful voltages for sputter-depositing catalysts range from about 50 volts
10 (V) to about 2 kilovolts (KV). The voltage differential charges the target 4 and holds the target 4 at a positive potential. The voltage differential also ionizes the gas 18. As the voltage differential increases, a plasma 22 (the charged target/plasma being conceptually illustrated
15 by reference numeral 22) forms on the target 4 as a result of a flux of the high-energy ions bombarding the target 4 surface. The high-energy ions eject or sputter atoms 24 from the target 4. The dislodged atoms 24 may be charged or uncharged. Some of these dislodged atoms
20 24 contact the substrate 6 and attach thereto. Thus, the atoms 24 form a coating 26 disposed about an exposed surface 28 of the substrate 6. It is to be understood that the coating 26 can attain multiple morphologies (described in detail below) that are dependent upon the
25 sputter-deposition conditions used. After the sputter-deposition process is complete, the power supply 20 is turned off and the chamber space 14 is returned to ambient pressure. At this point, the now sputter-coated substrate 6 is removed. Radiofrequency magnetrons will
30 also generate a useful plasma 22 that will sputter-deposit atoms 24.

It is to be understood that the substrate 6 may be coated on more than one surface and that each surface may

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be coated with alternative target 4 materials. For example, electrolyte membranes used for constructing MEAs typically have at least two surfaces that are referred to as an eventual anode side of the membrane and an eventual cathode side of the membrane. It can be advantageous to sputter-deposit different targets 4 on the eventual anode side and the eventual cathode side of the membrane. A preferred example of such an sputter-coated electrolyte membrane having different catalysts on the eventual anode side and the eventual cathode side is a NAFION (TM)-based membrane sputter-coated on the eventual anode side of the membrane with platinum and ruthenium and sputter-coated on the eventual cathode side of the membrane with Platinum. Alternatively, some membranes, e.g., membranes for use in H₂/air fuel cells, may incorporate identical substrates 6 on each side.

The coating 26 morphology includes the microscopic and macroscopic appearance of the coating 26 as well as the sputter-deposited coating 26 thickness. The sputter-deposited coating morphology is affected by numerous parameters including the voltage differential, the chamber space 14 pressure, the length of the sputter-deposition process, the substrate 6 material, and the target 4 material. Changing the sputter-deposition conditions such as the sputter rate, chamber pressure, and voltage influence the coating 26 grain size, composition, crystallinity, porosity, and surface area. Typically, high gas pressures lead to more porous deposits and low pressures result in compact fine grained sputter-coatings 26. Also, fine-grained sputter-coatings 26 can occur when using high deposition rates. Lower deposition rates favor large and porous coatings 26. Increased voltages increase target deposition rates and

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tend to produce more fine-grained deposits. Coating morphologies are also affected by the gas 18 pressure. The optimum conditions will vary according to the target 4 and the desired coating 26 morphology and should be 5 determined empirically.

Alternative morphologies are achieved by selecting different target 4 materials and/or altering the sequence of sputter-depositing the target 4 materials. For example, using platinum as the target 4 results in a 10 different coating than a mixture or alloy of platinum and ruthenium. Additionally, sputter-depositing platinum and ruthenium concurrently from two different target 4 sources results in a different coating than sputter-depositing platinum and ruthenium in a sequential 15 fashion. For example, platinum and ruthenium sources placed concurrently in the same sputter-deposition chamber 2 and used as multiple targets 4 will deposit platinum and ruthenium as a composite coating 26. Alternatively, a substrate 6 sputter-deposited with a 20 first platinum target 4 material and then further sputter-deposited with a second ruthenium target 4 material leads to layers of platinum and ruthenium. Altering the morphology and the sputter-deposited coating thickness will alter MEA performance characteristics.

25 Preferably, the sputter-deposition process results in a sputter-deposited coating weight or loading that ranges from about 0.05 mg of the target 4 per square centimeter of exposed substrate surface 28 to about 1.0 mg of target 4 per square centimeter of exposed substrate 30 surface 28. Other sputter-deposited coating weights or loads include less than about 0.05 mg of the target 4 per square centimeter of exposed substrate surface 28, less than about 0.1 mg of the target 4 per square centimeter

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of exposed substrate surface 28, less than about 0.5 mg of the target 4 per square centimeter of exposed substrate surface 28, and less than about 0.7 mg of the target 4 per square centimeter of exposed substrate surface 28. Excessive coating 26 weights result in thicker coatings that decrease fuel cell performance. Therefore, coatings 26 less than about 1.0 mg of target 4 per square centimeter of exposed substrate surface 28 are desirable. Typically, effective catalyst layers or coatings are achieved by allowing the sputter-deposition process to proceed from about 1000 seconds to about 10,000 seconds at a voltage differential from about 50 V to about 2 KV at a pressure from about 2 millitorr to about 200 millitorr.

15 The sputter-deposited coating 26 thickness can be determined using any method, including using scanning electron microscope methods and/or a Rutherford back scattering spectrophotometer methods. An illustrative method for determining the sputter-deposited coating thickness includes weighing the substrate 6 before and after the sputter-deposition process. The substrate 6 weight increase will correspond to the weight of the sputter-deposited target 4. The surface area of the substrate 6 is determined by computing the surface area of the substrate 6 that was exposed to sputter-deposition in the sputter-depositing chamber 2. The density of the target 4 material is then used to estimate coating 26 thickness.

30 Targets 4 may be sputter-deposited onto an anode carrier, a cathode carrier, carbon paper, or other suitable material. The resulting sputter-coated carrier or paper materials are used to fabricate MEAs. Carrier materials useful for fabricating anodes and cathodes and

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methods for preparing the carrier materials, including methods to alter the wettability of the carriers, are known. To use the methods described herein to prepare an electrode, a suitable carrier such as carbon paper is
5 suitably secured to the substrate holder 8. Once secured, the suitable carrier is sputter-coated using any of the target 4 materials disclosed herein by following the methods described for sputter-coating electrolyte membranes. For example, if an anode is being
10 constructed, the target 4 material should contain catalysts appropriate for the anode such as a platinum-ruthenium alloy. Alternatively, if a cathode surface is being produced, the target 4 material should contain catalysts appropriate for the cathode such as platinum.
15 Other useful target materials include Ni, Ti, Zr, Sn, SnO₂, Ru, Pt, Os, Ir, W, WO₃, Re, Pd, Mo, Nb, RuO₂, alloys thereof, and other similar materials.

Sputter-coated membranes, anode carriers, cathode carriers, carbon paper, and other suitable sputter-coated
20 materials are fabricated into membrane electrode assemblies (MEA) for use in fuel cells. For example, electrolyte membranes such as NAFION (TM) are sputter-coated with a catalyst on one or more sides. The sputter-coated membrane is bonded or suitably secured to
25 an anode and a cathode. Bonding methods include known hot-pressing techniques. The anode and/or cathode can also be prepared using the above-described sputter-depositing method before being assembled into a MEA. Alternatively, the anode and/or cathode are prepared by
30 conventional painting, spraying, or other methods. Additionally, the anode and/or cathode may be constructed from a noncatalytic conductive material such as gold. An

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MEA is then assembled into a fuel cell or fuel cell test fixture, which is useful for evaluating MEA performance.

The membranes, electrodes and methods disclosed herein may work in any type of fuel cells including
5 polymer electrolyte fuel cells, phosphoric acid fuel cells, alkaline fuel cells, molten-carbonate fuel cells, and solid oxide fuel cells by sputter-depositing using known catalysts and known membranes. For example, the methods disclosed herein are useful for preparing MEAs
10 used in methanol fuel cells and hydrogen fuel cells.

Example 1. Evaluating Fuel Cells Using
Sputter-deposited Anodes.

NAFION (TM) 117 was cast into a membrane using known methods. The hydrated membrane was allowed to air
15 dry for 24 hours and then vacuum dried from about 8 to about 24 hours. The vacuum-dried membrane was weighed and secured in a substrate holder of a sputter-deposition chamber with the eventual anode side of the membrane being exposed. A platinum-ruthenium target source was
20 secured to a target holder. The sputter-depositing chamber was evacuated and pressurized with 10-15 millitorr of argon gas. The membrane was sputter-deposited for 1000 seconds with a voltage differential of 1 KV. The membrane was then re-weighed. The sputter-
25 coating was 0.5 mg/cm² of the anode side of the membrane.

A carbon paper carrier was secured in the sputter-depositing chamber as described above. The carrier was coated with 0.5 mg/cm² of the platinum-ruthenium target source according to the methods used above to coat the
30 membrane. A cathode electrode was assembled using known techniques.

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The membrane and electrodes were then assembled into a membrane electrode assembly for use in a direct methanol fuel cell test fixture using known hot-pressing techniques at 140-150°C.

5 FIG. 2 depicts the results of the electrical performance of the fuel cell test fixture in a 0.5 M methanol fuel source and a 1.0 M methanol fuel cell. Each fuel cell was run under an external load held at a constant current, 20 psig oxygen concentration, at 85°C.

10 Example 2. Evaluating Sputter-deposited Catalyst Materials

Membranes, electrodes, and a fuel cell test fixture were fabricated as indicated in Example 1. Platinum and platinum/ruthenium target sources were used
15 to prepare a platinum anode and a platinum/ruthenium anode, respectively.

The fuel cell fixtures were used to evaluate the two anodes. Anodes were evaluated using known methods. FIG. 3 depicts the differences in the polarization
20 characteristics of platinum and platinum/ruthenium sputter-deposited anode electrodes deposited at 1 mg/cm², i.e., 0.5 mg/cm² deposited on the membrane and 0.5 mg/cm² deposited on the anode.

25 Example 3. Comparing Sputter-deposited Electrodes and Conventional Electrodes

Sputter-deposited membranes, electrodes, and a fuel cell test fixture were fabricated as indicated in Example 1. The sputter-deposition resulted in the platinum/ruthenium target being deposited at 1 mg/cm² for
30 the anode side, i.e., 0.5 mg/cm² deposited on the membrane and 0.5 mg/cm² deposited on the anode. A fuel cell test

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fixture was also fabricated from membranes and electrodes fabricated using conventional catalyst painting techniques to apply a platinum/ruthenium catalyst to an anode electrode. The conventional anode electrode had a catalyst ink applied at 8 mg/cm².

The membrane electrode assemblies were assembled into conventional methanol fuel cell test fixtures. The fuel cells were compared at different constant currents using a 1 M methanol fuel source, 20 psig oxygen at 85°C. FIG. 4 depicts the comparison of the sputter-coated and conventional electrode performance in the fuel cells.

Example 4. Computing Catalyst Utilization
for Different Catalyst Layers

Catalyst utilization for the catalyst coating methods were computed and compared. FIG. 5 depicts a catalyst utilization curve for sputter-deposited catalyst layers, carbon-supported catalyst ink coatings, and unsupported catalyst ink coatings. Referring to FIG. 5, sputter-deposited catalysts result in good electrical performance and the highest power density per milligram of catalyst used, which represents the highest catalyst utilization. A fuel cell voltage of 0.45 V at 300 mA/cm² and current densities as high as 1 A/cm² can be sustained with fuel cells having sputter-deposited catalysts.

Other aspects, advantages, and modifications are within the scope of the following claims.

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What is claimed is:

1. A method for preparing a membrane for use in a fuel cell membrane electrode assembly comprising the steps of:
 - 5 providing an electrolyte membrane; and
sputter-depositing a catalyst onto said electrolyte membrane.
2. The method of claim 1, wherein said electrolyte membrane further comprises at least a first
10 side and a second side, and wherein said catalyst is applied to said first side and said second side of said electrolyte membrane.
3. The method of claim 1, wherein said sputter depositing of said catalyst results in a sputter-
15 deposited catalyst weight of less than about 1.0 mg of catalyst per square centimeter of said electrolyte membrane.
4. The method of claim 1, wherein said sputter depositing of said catalyst results in a sputter-
20 deposited catalyst weight of less than about 0.05 mg of catalyst per square centimeter of electrolyte membrane.
5. The method of claim 1, wherein said sputter depositing of said catalyst results in a sputter-
deposited catalyst weight from about 0.05 mg of catalyst
25 per square centimeter of said electrolyte membrane to about 1.0 mg of catalyst per square centimeter of said electrolyte membrane.

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6. The method of claim 1, wherein said catalyst is sputter-deposited to an anode side of said electrolyte membrane.

7. The method of claim 6, wherein said sputter
5 depositing of said catalyst results in a sputter-deposited catalyst weight from about 0.05 mg of catalyst per square centimeter of said anode side of said electrolyte membrane to about 1.0 mg of catalyst per square centimeter of said anode side of said electrolyte
10 membrane.

8. The method of claim 1, wherein said catalyst is sputter-deposited to a cathode side of said electrolyte membrane.

9. The method of claim 8, wherein said sputter
15 depositing of said catalyst results in a sputter-deposited catalyst weight from about 0.05 mg of catalyst per square centimeter of said cathode side of said electrolyte membrane to about 1.0 mg of catalyst per square centimeter of said cathode side of said
20 electrolyte membrane.

10. The method of claim 1, wherein said catalyst is sputter-deposited to an anode side of said electrolyte membrane and said catalyst is sputter-deposited to a cathode side of said electrolyte membrane.

25 11. The method of claim 10, wherein said sputter depositing of said catalyst results in a sputter-deposited catalyst weight from about 0.05 mg per square

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centimeter of said electrode membrane to about 1.0 mg per square centimeter of said electrode membrane.

12. The method of claim 1, wherein said catalyst comprises a transition metal.

5 13. The method of claim 1, wherein said catalyst is selected from the group consisting of Pt, Ru, Ni, Ti, Zr, Sn, SnO₂, Os, Ir, W, WO₃, Pd, Mo, Nb, RuO₂, and Re.

14. The method of claim 1, wherein said catalyst is sputter-deposited from an alloy.

10 15. The method of claim 1, wherein said catalyst further comprises two or more catalysts.

16. The method of claim 15, wherein said catalysts comprise transition metals.

15 17. The method of claim 15, wherein said catalysts are selected from the group consisting of Pt, Ru, Ni, Ti, Zr, Sn, SnO₂, Os, Ir, W, WO₃, Pd, Mo, Nb, RuO₂, and Re.

18. The method of claim 15, wherein said two or more catalysts are sputter-deposited from an alloy.

20 19. The method of claim 15, wherein said two or more catalysts are sputter-deposited as layers.

20. The method of claim 15, wherein said two or more catalysts are sputter-deposited at the same time.

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21. The method of claim 1, wherein said electrolyte membrane further comprises a first side and a second side, wherein said catalyst further comprises two or more catalysts, and wherein said two or more catalysts
5 are sputter-deposited to at least one side of said electrolyte membrane.

22. A method for forming an electrode for use in a fuel cell membrane electrode assembly comprising the steps of:
10 obtaining a catalyst;
obtaining a backing; and
sputter-depositing said catalyst onto said backing.

23. The method of claim 22, wherein said backing
15 comprises carbon paper.

24. The method of claim 22, wherein said sputter depositing of said catalyst results in a sputter-deposited catalyst weight of less than about 1.0 mg of catalyst per square centimeter of said backing.

20 25. The method of claim 22, wherein said sputter depositing of said catalyst results in a sputter-deposited catalyst weight of less than about 0.05 mg of catalyst per square centimeter of backing.

25 26. The method of claim 22, wherein said sputter depositing of said catalyst results in a sputter-deposited catalyst weight from about 0.05 mg of catalyst per square centimeter of said backing to about 1.0 mg of catalyst per square centimeter of said backing.

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27. The method of claim 22, wherein said catalyst is sputter-deposited to an anode electrode.

28. The method of claim 22, wherein said catalyst is sputter-deposited to a cathode electrode.

5 29. The method of claim 22, wherein said catalyst comprises a transition metal.

30. The method of claim 22, wherein said catalyst is selected from said group consisting of Pt, Ru, Ni, Ti, Zr, Sn, SnO₂, Os, Ir, W, WO₃, and Re.

10 31. The method of claim 22, wherein said catalyst is sputter-deposited from an alloy.

32. The method of claim 22, wherein said catalyst further comprises two or more catalysts.

15 33. The method of claim 32, wherein said catalysts comprise transition metals.

34. The method of claim 32, wherein said catalysts are selected from said group consisting of Pt, Ru, Ni, Ti, Zr, Sn, SnO₂, Os, Ir, W, WO₃, and Re.

20 35. The method of claim 32, wherein said two or more catalysts are sputter-deposited from an alloy.

36. The method of claim 32, wherein said two or more catalysts are sputter-deposited as layers.

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37. The method of claim 32, wherein said two or more catalysts are sputter-deposited at the same time.

38. A fuel cell comprising:
an anode electrode;
5 a cathode electrode;
a fuel supply; and
an electrolyte membrane, wherein said electrolyte membrane further comprises a sputter-deposited catalyst, said sputter-deposited catalyst effective for sustaining
10 a voltage across a membrane electrode assembly in said fuel cell.

39. The fuel cell of claim 38, wherein said sputter-deposited catalyst weight is less than about 1.0 mg of catalyst per square centimeter of said electrolyte
15 membrane.

40. The fuel cell of claim 38, wherein said sputter-deposited catalyst weight is less than about 0.05 mg of catalyst per square centimeter of said electrolyte membrane.

20 41. The fuel cell of claim 38, wherein said sputter-deposited catalyst weight is from about 0.05 mg of catalyst per square centimeter of said electrolyte membrane to about 1.0 mg of catalyst per square centimeter of said electrolyte membrane.

25 42. The fuel cell of claim 38, wherein said catalyst is sputter-deposited to an anode side of said electrolyte membrane.

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43. The fuel cell of claim 38, wherein said sputter depositing of said catalyst results in a sputter-deposited catalyst weight from about 0.05 mg of catalyst per square centimeter of said anode side of said electrolyte membrane to about 1.0 mg of catalyst per square centimeter of said anode side of said electrolyte membrane.

44. The fuel cell of claim 38, wherein said catalyst is sputter-deposited to a cathode side of said electrolyte membrane.

45. The fuel cell of claim 38, wherein said sputter depositing of said catalyst results in a sputter-deposited catalyst weight from about 0.05 mg of catalyst per square centimeter of said cathode side of said electrolyte membrane to about 1.0 mg of catalyst per square centimeter of said cathode side of said electrolyte membrane.

46. The fuel cell of claim 38, wherein said catalyst is sputter-deposited to an anode side of said electrolyte membrane and said catalyst is sputter-deposited to a cathode side of said electrolyte membrane.

47. The fuel cell of claim 38, wherein said catalyst comprises a transition metal.

48. The fuel cell of claim 47, wherein said catalyst is selected from the group consisting of Pt, Ru, Ni, Ti, Zr, Sn, SnO₂, Os, Ir, W, WO₃, and Re.

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49. The fuel cell of claim 38, wherein said catalyst is sputter-deposited from an alloy.

50. The fuel cell of claim 38, wherein said catalyst further comprises two or more catalysts.

5 51. The fuel cell of claim 50, wherein said catalysts comprise transition metals.

52. The fuel cell of claim 50, wherein said catalysts are selected from the group consisting of Pt, Ru, Ni, Ti, Zr, Sn, SnO₂, Os, Ir, W, WO₃, and Re.

10 53. The fuel cell of claim 50, wherein said two or more catalysts are sputter-deposited from an alloy.

54. The fuel cell of claim 50, wherein said two or more catalysts are sputter-deposited as layers.

15 55. The fuel cell of claim 50, wherein said two or more catalysts are sputter-deposited at the same time.

56. The fuel cell of claim 38, wherein said electrolyte membrane further comprises a first side and a second side, wherein said catalyst further comprises two or more catalysts, and wherein said two or more catalysts
20 are sputter-deposited to at least one side of said electrolyte membrane.

57. The fuel cell of claim 38, said anode electrode further comprising a sputter-deposited catalyst.

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58. The fuel cell of claim 38, said cathode electrode further comprising a sputter-deposited catalyst.

59. The fuel cell of claim 38, wherein said fuel
5 cell comprises a methanol fuel cell.

60. The fuel cell of claim 38, wherein said fuel cell comprises a hydrogen fuel cell.

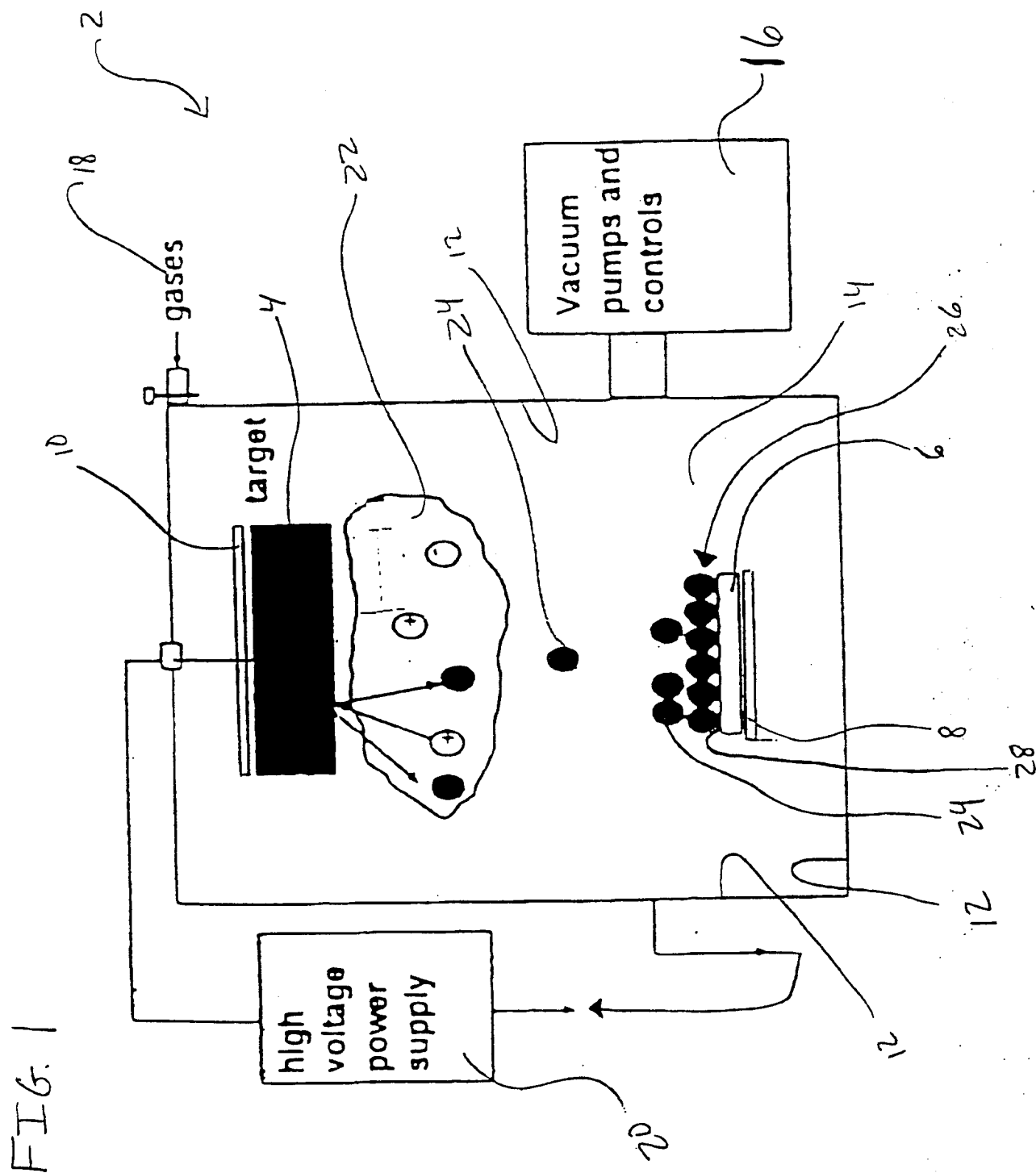


FIG. 2

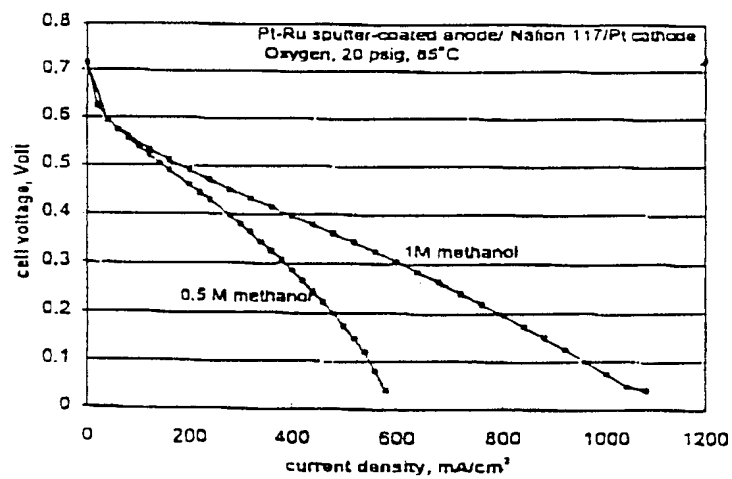


FIG. 3

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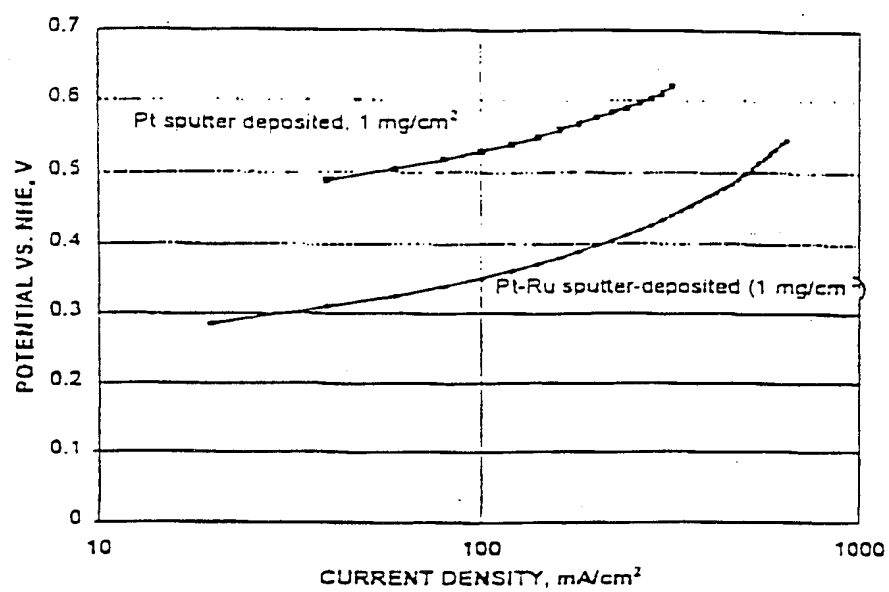
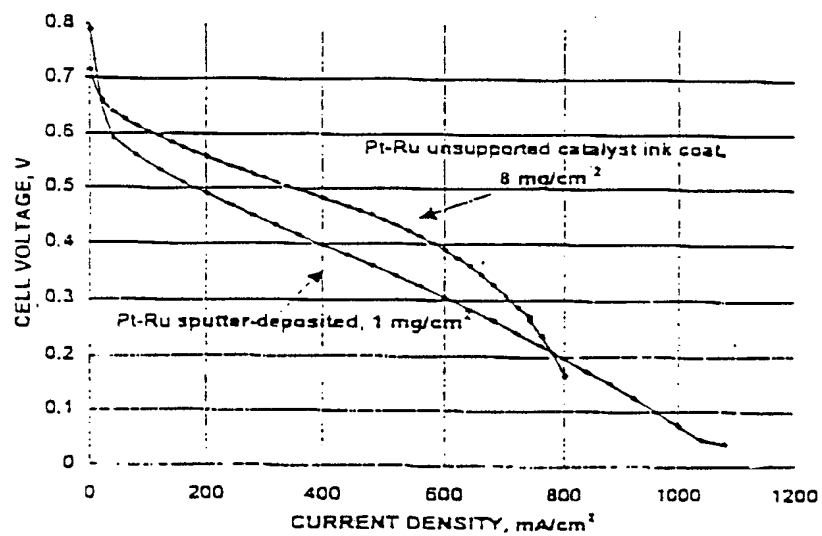


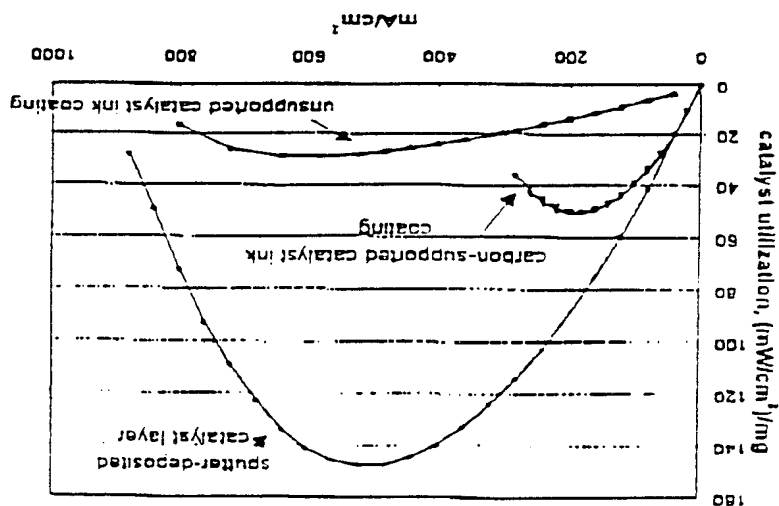
FIG. 4

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FIG. 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/19838

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : H01M 4/88; C23C 14/00

US CL : 429/44; 204/192.14; 502/101

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/30, 44; 204/192.14, 192.15, 192.29; 502/101

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DERWENT WORLD PATENTS on ORBIT

search terms: Derwent manual code L03-c04, sputtering

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US 5,750,013 A (LIN) 12 May 1998, col. 2, line 28-col. 5, line 14.	1-60
X	US 5,277,996 A (MARCHETTI et al) 11 January 1994, col. 5, lines 8-45.	22, 24-30
A	US 4,275,126 A (BERGMANN et al) 23 June 1981, col. 3, line 65-col. 4, line 12.	1-60
X	JAPIO Abstract No. 92-162,362 for JP4-162,362 (HIRATA et al) 05 June 1992, abstract, lines 1-12.	22-30
A	US 5,242,764 A (DHAR) 07 September 1993, col. 2, lines 41-61.	1-60
A	US 5,512,152 A (SCHICHT et al) 30 April 1996, col. 2, lines 11-21.	13, 17, 30, 34, 48, 52



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
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Date of the actual completion of the international search

02 DECEMBER 1998

Date of mailing of the international search report

04 JAN 1999

Name and mailing address of the ISA/US
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Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

STEPHEN J. KALAFUT

Telephone No. (703) 308-0661

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International application No.
PCT/US98/19838

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,882,232 A (BUGNET et al) 21 November 1989, col. 2, lines 22-35.	22-37
A	US 5,641,586 A (WILSON) 24 June 1997, col. 3, lines 6-22.	1-60